Improved Mechanical Properties of Chemically Amplified, Positive Tone, Polynorbornene Dielectric

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The mechanical properties of an aqueous developed, chemically amplified, polynorbornene-based permanent dielectric have been investigated. The previously reported hexafluoroisopropanol norbornene and tert-butyl ester norbornene copolymer has been modified via two routes to improve the mechanical properties of the polymer and enable thick-film deposition. First, a third monomer, butyl norbornene (ButylNB) was added to the polymer backbone. The inclusion of 24 mol% ButylNB lowered the elastic modulus from 2.64 to 2.35 GPa and raised the dielectric constant from 2.78 to 3.48. The second approach added a low molecular weight, plasticizing additive in the copolymer formulation. Many additives were immiscible with the resin or did not affect the mechanical properties. Trimethyololpropane ethoxylate (TMPEO) was found to be a miscible additive that improved mechanical properties and could participate in crosslinking the final dielectric material. TMPEO interacted with the PAG, lowering its decomposition temperature. An optimal formulation and processing scheme were determined. A formulation with 10 pphr TMPEO was measured to have a dielectric constant of 2.94, an elastic modulus of 1.95 GPa, a sensitivity at 365 nm of 175 mJ/cm^2, and a contrast of 4.36.
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Photo-definable, permanent, low-k dielectrics are widely used in the fabrication of microelectronic devices and packages.[1-5] These dielectrics electrically isolate the interconnect and mechanically stabilize the structures for the life of the device. On integrated circuits, organic dielectrics can be used for interlayer isolation and/or the stress buffer layer on top of the device. Stress buffer layers protect the top surface of the chip and can mitigate mechanical failures that arise from a mismatch of the coefficient of thermal expansion between the chip and package during thermal cycling. In microelectronics packages, low-k dielectrics can be used in the buildup layers, electrically separating the electrical conductors. Low permittivity is critical for use in these applications, as it affects device performance, energy loss, and signal integrity.

Photo-definability is an attractive property for permanent polymeric dielectrics. The ability to directly pattern the dielectric by photolithographic techniques mitigates the need for a separate photoresist and pattern transfer steps. This can lower the overall fabrication cost and reduce the number of individual process steps.[2] For stress buffer and redistribution applications, positive tone photo-definable dielectrics are more desirable than negative tone ones because the lithographic mask is mostly opaque mask and less prone to transfer particle defects. Also, holes and lines in positive tone materials exhibit sloped sidewalls (opening wider at the top) which is beneficial for void-free plating of the copper interconnects. Aqueous developability is another attractive property, as it mitigates the need for environmentally harmful organic solvent developers. Further, the dielectric should exhibit high sensitivity and contrast for high throughput and high quality feature patterning.

Previously, a chemically amplified, positive tone, permanent polynorbornene (PNB) dielectric was reported.[6] This dielectric was composed of a copolymer of hexafluoroisopropanol norbornene (HFANB) and tert-butyl ester norbornene (TBENB). The chemical structure of this polymer is shown in Figure 1. Positive tone photo-definability was achieved with a chemically amplified solubility switching mechanism in which a photo-generated acid catalyzed the deprotection of TBENB to produce a carboxylic acid that was soluble in aqueous tetramethylammonium hydroxide (TMAH) developer. Excellent lithographic properties were reported as a result of the acid-catalyzed photochemistry. The minimum dose to achieve complete polymer solubility (D_{100}) was measured to be 8.09 mJ/cm^2 at 248 nm radiation. The contrast was measured to be $\geq$14.2. These lithographic values are more than an order of magnitude better than those reported for other positive tone dielectrics.[7,8] Mechanical and electrical properties of this dielectric were also evaluated. A formulation with 60/40 mol% HFANB/TBENB exhibited a dielectric constant of 2.78 and an elastic modulus of 2.60 GPa. These properties make this polymer well-suited for use as a low-k dielectric.

Though the chemically amplified PNB dielectric had excellent properties, the dielectric exhibited cracking when coated to thickness greater than ~3 μm on silicon wafers. This result is due to a combination of phenomena. First, the coefficient of thermal expansion (CTE) of the polymer (39.5 ppm/K) is not well-matched to silicon (3 ppm/K). This mismatch produces thermal stresses in the film upon cooling after the baking and curing steps. It is noted that other PNB dielectrics with similar CTEs have been deposited crack-free on silicon wafers at much greater thicknesses.[9,10] The difference between the chemically amplified dielectric and previous PNB dielectrics is the presence of the TBENB. During polymer synthesis, the presence of TBENB slows the polymerization, and limits the obtainable molecular weight to ~50 kg/mol. Since PNB polymers have a helical conformation, this molecular weight is not high enough to induce chain-to-chain entanglement, resulting in low toughness values for the polymer.[11,12] The mismatched CTE between the polymer and silicon along with low toughness led to cracking of thick films. Although uses on polymer-based substrates, such as printed circuit boards, would lower the CTE mismatch and cracking, there is interest in improving the mechanical toughness of the chemically amplified, photo-definable polynorbornene.

In this paper, two approaches to improving the mechanical toughness of the chemically amplified PNB dielectric were investigated. First, a terpolymer of HFANB, TBENB, and a third monomer, butyl norbornene (ButylNB) was synthesized. The structure of the terpolymer is shown in Figure 1. In addition to possibly improving the toughness, the inclusion of an aliphatic pendent group may also lower the dielectric constant of the final film because it is a less polar moiety than the other substituents on the polymer backbone. The second approach to improving the toughness of the HFANB/TBENB copolymer was to include a plasticizing additive to the formulation. Several plasticizing additives for controlling the polymer toughness were evaluated including poly(ethylene glycol) methyl ether (PEGME, Mn ~550 g/mol), trimethylolpropane (TMP), trimethylolpropane ethoxylate (TMPEO, Mn ~450 g/mol), pentaerythritol, and pentaerythritol ethoxylate (Mn ~270 g/mol). The structures are shown in Figure 2. PEGME was investiged in more detail as a non-reactive additive (i.e. does not

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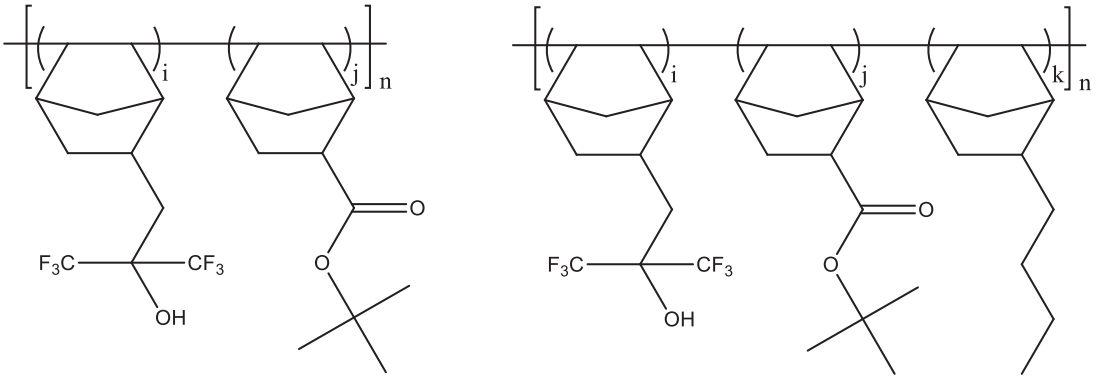

Figure 1. Chemical structure of HFANB-TBENB copolymer (left) and HFANB-TBENB-ButylNB terpolymer (right).

participate in polymer cross-linking). The other four additives have alcohol functionalities which can cross-link via the Fischer esterification curing mechanism. The additives vary in alcohol functionality (three alcohols vs. four alcohols) and molecular weight. Formulations with high miscibility were tested for mechanical and electrical properties to determine the effect of the variation on the final properties, including mechanical and lithographic properties.

Experimental

PNB polymers were donated by Promerus, LLC (Brecksville, OH). Monomer ratios of the copolymers and terpolymers are listed in Table I. For example, PNB-E is a terpolymer of 43/47/10 mol% HFANB/TBENB/ButylNB. All polymers had a weight average molecular weight of approximately 40 kg/mol. Mixtures of the norbornene polymers were made with a photoacid generator (PAG), 4-methylphenyl[4-(1-methylethyl)phenyl] tetrakis(pentafluorophenyl) borate (Rhodorsil FABA). PAG was added at 3 mass parts PAG per 100 mass parts polymer (pphr). The PAG was active at 248 nm radiation. To sensitize the dielectric to 365 nm, 1-chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) was added at 1 pphr. Films were solvent-cast from propylene glycol monomethyl ether acetate (PGMEA) by spin-coating at various speeds from 1500 to 3000 rpm for 60 sec. The PNB films were spin-coated using a CEE 100CB spin-coater. Films were soft baked at 100°C for 60 s to remove residual PGMEA. Photolithographic exposures were performed on an Oriel Instruments flood exposure source with a 1000 W Hg(Xe) lamp filtered to 365 nm radiation. Films were post-exposure baked (PEB) at 140°C for various times. Films were developed in MF-319, a 0.26 N TMAH developer. Films were cured in a Lindberg quartz tube furnace at 250°C for 2 hr under a nitrogen atmosphere. The temperature of the oven was ramped to 250°C from ambient temperature over a 65 min period.

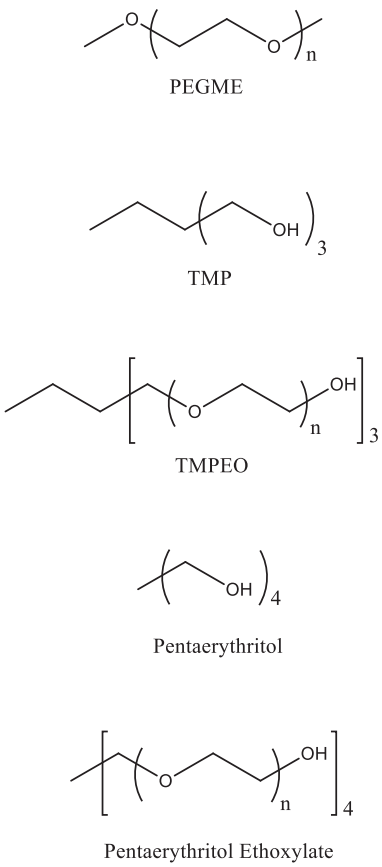

Figure 2. Chemical stuctures of plasticizing additives.

For mechanical property measurements, films were cast on 100 mm ⟨100⟩ silicon wafers. Elastic modulus was measured with a Hysitron Triboindenter. Samples of approximately 2 μm thickness were indented nine times each at depths of 100 to 200 nm, which is less than 10% of the film thickness.[13] Indents were performed with a cube corner diamond tip (northstar, tip radius ~40 nm) and calibrated against quartz and polycarbonate standards. The corrected tip geometry was defined by Equation 1, where h_c is the contact depth, $A(h_c)$ is the projected contact area at a specific h_c, and C_1-C_8 are fitted coefficients to account for tip imperfections. Step times for each indent were held constant, while the peak force was varied. The tip was loaded over a 10 s period of time, held at the peak force for 10 s to allow for time-dependent relaxations, and unloaded over a 4 s period of time.[13] Hardness, H, was calculated at the maximum load, P_{max}, divided by $A(h_c)$, Equation 2. The contact depth was estimated using the Oliver Pharr model in Equation 3, where h_{max} is the maximum indent depth, ε, is a geometrical constant, and S is the stiffness.[14] The stiffness was defined as the initial slope of the unloading curve, and the reduced modulus (E_r) was calculated using Equation 4, where β is a geometrical constant. The elastic modulus of the film (E_f) was calculated using Equation 5, where E_i is the elastic modulus of the diamond tip

Table I. Monomer ratios of PNB polymers.

	Mol %		
Polymer	HFANB	TBENB	ButylNB
PNB-A	70	30	0
PNB-B	50	50	0
PNB-C	35	65	0
PNB-D	0	100	0
PNB-E	43	47	10
PNB-F	38	38	24

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(1140 GPa), and ν_f and ν_i are the Poisson's ratios of the film and tip, respectively. ν_f was assumed to be 0.33, and ν_i was 0.07.

$$A(h_c) = 2.598h_c^2 + C_1h_c^1 + C_2h_c^{1/2} + \ldots + C_8h_c^{1/128} \quad [1]$$

$$H = \frac{P_{max}}{A(h_c)} \quad [2]$$

$$h_c = h_{max} - \frac{\varepsilon P_{max}}{S} \quad [3]$$

$$E_r = \frac{\sqrt{\pi}}{2\beta}\frac{S}{\sqrt{A(h_c)}} \quad [4]$$

$$\frac{1}{E_r} = \frac{\left(1-v_f^2\right)}{E_f} + \frac{\left(1-v_i^2\right)}{E_i} \quad [5]$$

The electrical properties of the films were measured by fabricating parallel plate capacitors. Substrates were prepared by first growing 500 nm of thermal oxide on the silicon wafers for electrical insulation. Aluminum was deposited by electron beam evaporation using a Kurt Lesker PVD75 to a thickness of 300 nm as measured by a quartz crystal microbalance (QCM). Films were spin-cast and cured by the same processes as stated above. To deposit the top aluminum pads, aluminum was evaporated onto the top of the sample through a molybdenum shadow mask with 1 mm diameter holes. Samples were dried at 150°C for 3 hr immediately prior to measuring the capacitance, C. The capacitance was measured at 200 kHz with a GW Instek LCR-800 on a Karl Suss probe station using a parallel RC model. The dielectric constant (i.e. real part of the complex permittivity), ε_r, was calculated from Equations 6 and 7, where ε_o is the permittivity of free space, t is the dielectric thickness, and A is the area of the aluminum pad. The dielectric constant was corrected for fringing fields with ASTM standard D150-11 by calculating an edge capacitance, C_e, based on the approximate dielectric constant, ε_r, thickness, t, and perimeter, P.[15] The edge capacitance was then subtracted from the original capacitance, and a new dielectric constant was calculated.

$$C = \frac{\varepsilon_o\varepsilon_r A}{t} \quad [6]$$

$$C_e = (0.0041\varepsilon_r' - 0.00334\ln(t) + 0.0122)P \quad [7]$$

Thermogravimetric analysis (TGA) was performed with a TA Instruments TGA Q50. TGA samples were heated at the same heating rate used for thermal curing, 3.54°C/min to a final temperature of 250°C. Dissolution rate experiments were performed using a QCM200 system (Stanford Research Systems). Samples were spin-coated onto a 1″ quartz crystal with 5 MHz unloaded resonant frequency and 0.4 cm^2 active surface area. Coated QCMs were developed with MF-319 in a 125 μL flow cell connected to an 800 μL/min peristaltic pump (Thermo Scientific). The flow path was equipped with a manual valve positioned ~5 cm from the inlet of the flow cell to control selection fluid (water or MF-319) impinging on the QCM. The polymer-coated QCM samples were first equilibrated in water before introduction of the aqueous base developer in order to minimize sharp frequency and resistance changes that result from immersion of the QCM into a viscous medium from air. Mass changes (Δm) were obtained by correlation of the resonant frequency change (Δf) using the Sauerbrey equation, Equation 8.

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad [8]$$

In Eq. 8, f_o is the resonant frequency of the unloaded quartz crystal, A is the active area between the gold electrodes, ρ_q is the density of quartz, and μ_q is the shear modulus of quartz.

For lithographic property measurements, silicon wafers were coated with a layer of bisphenol-A diglycidyl ether epoxy (BPADGE) to improve adhesion of the polymer. 2-ethyl-4-methylimidazole was added as a curing agent to the BPADGE, and the epoxy films were cured under nitrogen for 2 hrs at 200°C. PNB films were cast onto the silicon/epoxy substrates by the same process as described above. The contrast and sensitivity of the optical exposure were measured by exposing the film through a variable density optical mask (Opto-line International Inc.). The contrast (γ) was calculated by plotting the normalized film thickness after an aqueous base develop vs. the logarithmic exposure dose and fitting a line to the points nearest D_{100}, Equation 9. D_{100} is the lowest dose at full development and D_0 is the maximum dose where no appreciable dissolution occurred. D_{100} and D_0 were calculated by extrapolating the slope of the contrast curve to a normalized thickness of 0 and 1, respectively.

$$\gamma = \frac{1}{\log\left(D_{100}/D_0\right)} \quad [9]$$

Results and Discussion

HFANB/TBENB/ButylNB terpolymer.— The elastic moduli and hardness of chemically amplified, PNB terpolymers were measured by indentation. In Figure 3, the modulus of PNB-B, PNB-E, and PNB-F are plotted with respect to the ButylNB mole fraction holding the HFANB/TBENB ratio constant at approximately 50/50 mol%. It can be seen that the introduction of the ButylNB monomer into the terpolymer lowers the modulus and hardness, and this change in mechanical properties is a function of the amount of ButylNB substituted. For the 50/50 mol% copolymer of HFANB/TBENB, the modulus and hardness are 2.64 GPa and 0.287 GPa, respectively. The terpolymer of 24 mol% ButylNB HFANB/TBENB polymer resulted in a lower modulus and hardness, 2.35 GPa and 0.205 GPa, respectively. This result may be due to several factors. First, the ButylNB could exhibit a low modulus due to the oily, butyl pendent groups. The inclusion of ButylNB into the polymer shifts the modulus closer to that of the ButylNB homopolymer. Second, HFANB and TBENB are functional

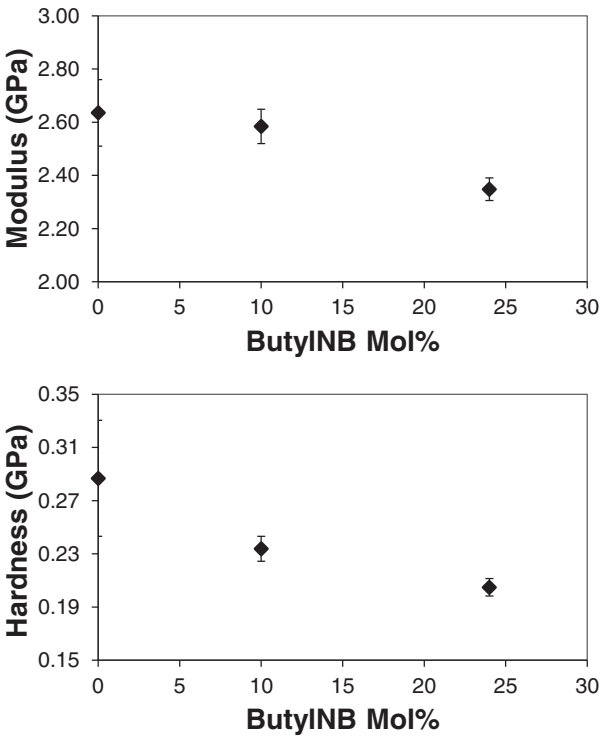

Figure 3. Modulus (top) and hardness (bottom) as a function of ButylNB content.

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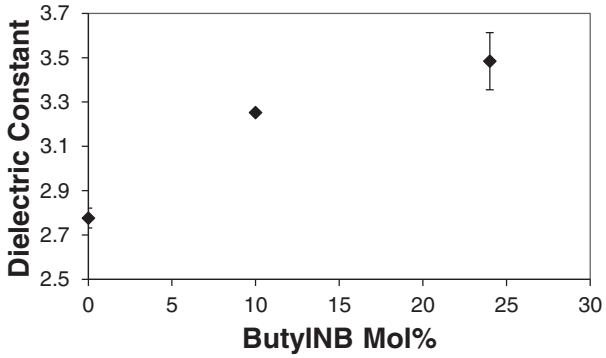

Figure 4. Dielectric constant as a function of ButylNB content in the HFANB/TBENB/ButylNB terpolymer.

pendent groups that can result in crosslinking of the polymer whereas the butyl substituent cannot participate in crosslinking. Thus, the inclusion of ButylNB likely results in lower crosslink density and lower elastic modulus since the modulus increases with crosslinking.

The dielectric constant of PNB terpolymers was measured in order to evaluate the effect of the ButylNB content on the electrical properties. Although ButylNB has a lower polarity than the other two monomers in the terpolymer, the dielectric constant increased with the inclusion of the ButylNB monomer in the terpolymer, as shown in Figure 4. Previous work showed that increasing the HFANB mol% in the copolymer decreased the dielectric constant, likely due to the low polarizability of the CF_3 moieties. It is likely, then, that replacement of the HFANB with ButylNB increases the dielectric constant because HFANB has a lower polarizability than ButylNB. The substitution led to an overall increase in the dielectric constant from 2.78 to 3.48. In addition, decreasing the concentration of the crosslinkable pendent groups (HFANB and TBENB) with ButylNB could result in a lower crosslink density after cure affecting the final film properties. Also, uncrosslinked acidic groups would increase the dielectric constant because they have high polarizability.

Plasticizing additives.— The addition of low molecular weight plasticizing additives to the polymers can be used to improve the thick-film mechanical properties. In evaluating potential additives, it was desired to understand how crosslink functionality (i.e. the ability of the additive to crosslink into the final structure) and molecular weight affect the material properties. Five additives were chosen for this purpose. PEGME was chosen as a nonfunctional additive that cannot crosslink. TMP and TMPEO were two trifunctional additives of different molecular weight. Pentaerythritol and pentaerythritol ethoxylate were tetrafunctional additives of different molecular weight. Five different formulations of PNB-C (35/65 mol% HFANB/TBENB) were made, each with a different additive. Formulations were mixed at 20 pphr of each additive. It was found that only PEGME, TMP, and TMPEO were visibly miscible with the PNB base polymer. Formulations with pentaerythritol and pentaerythritol ethoxylate had visible particles. Pentaerythritol and pentaerythritol ethoxylate are likely too hydrophilic for high miscibility with the hydrophobic polymer. However, it was undetermined whether these additives were completely immiscible or if a miscibility limit had been reached, so films were cast with each formulation and cured.

Films prepared with pentaerythritol ethoxylate were of poor quality after spin coating due to the immiscibility of the additive with the base polymer. Films prepared with PEGME produced good quality films after spinning and soft bake, but upon curing, an oily layer was observed on the surface of these samples. Later attempts to evaporate aluminum on PEGME-containing films proved difficult as the aluminum did not adhere to the oily film. It is likely that PEGME diffused out of the film to the surface at the elevated cure temperature. Curing of TMPEO-loaded films, on the other hand, produced high quality films with no oily film. This suggests that the alcohol groups on TMPEO participate in the cross-linking polymer reaction and are no longer mobile after curing.

The polymer films made with TMP, TMPEO, and pentaerythritol produced high quality films without cracks. The elastic modulus of the high quality films are compared to a control film with no additive. The modulus of the control film was 3.27 GPa, whereas films with TMP and pentaerythritol had a modulus of 3.38 GPa and 3.34 GPa, respectively. These are slightly higher than the value without additives, though the standard deviation of the measurement was measured to be ~0.09 GPa. This indicates that TMP and pentaerythritol had little influence on the mechanical properties. Pentaerythritol was immiscible with the solvated polymer, so it was not incorporated into the film. It is unknown whether TMP was incorporated into the film. A film with TMPEO was measured to have an elastic modulus of 2.69 GPa, which is a clear decrease from the value without additives. Additional testing was performed on TMPEO containing films since it was the only additive to lower the elastic modulus, completely dissolve into the starting mixtures, and produce high quality films.

Polymer formulations were prepared with PNB-A (70/30 mol% HFANB/TBENB) with various TMPEO loadings. The 70/30 polymer produced the lowest modulus and dielectric constant of the copolymers investigated in a previous work.[6] Mechanical properties of the TMPEO-loaded films were measured by nanoindentation. As seen in Figure 5, the elastic modulus of the film decreased from 2.47 to 1.80 GPa and the hardness decreased from 0.20 to 0.14 GPa with the addition of 20 pphr TMPEO. Films with 10 pphr TMPEO were coated to 4.8 um thickness without cracks. Minor cracking was seen at 5.7 um. Films with 15 and 20 pphr TMPEO did not exhibit cracking at any thicknesses attempted, up to 7.5 um. Without TMPEO, cracks were observed in all films greater than 3 μm thick.

The dielectric constant of the PNB-A formulations with TMPEO was measured. These results are given in Figure 6. The addition of 5 pphr TMPEO to PNB-A resulted in a slight decrease in the dielectric constant, however, the dielectric constant increased at higher TMPEO concentrations. Without TMPEO, cross-linking proceeds via the esterification reaction until the mobility of the polymer is sufficiently low

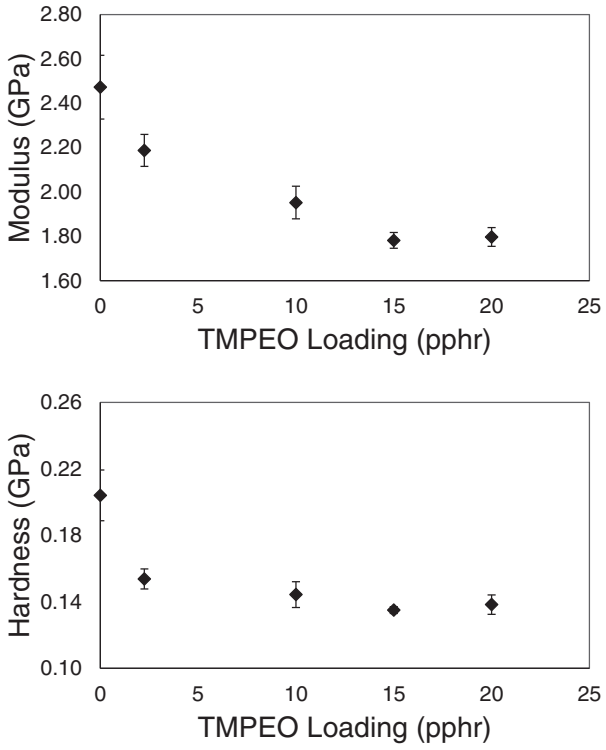

Figure 5. Effect of TMPEO on elastic modulus (top) and hardness (bottom) of PNB film.

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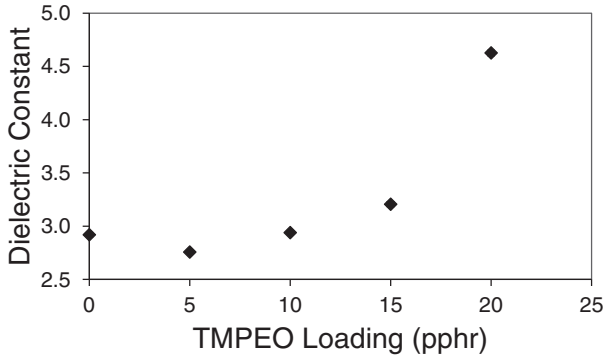

Figure 6. Effect of TMPEO on dielectric constant.

so as to prevent further reaction. The presence of TMPEO increases the mobility of reactive groups within the polymer matrix. The polarizability of the resulting ester is lower than that of the carboxylic acid reactant giving the ester product a lower dielectric constant. Increasing the loading of TMPEO shifts the alcohol-to-carboxylic acid ratio. When the ratio of alcohol-to-acid becomes too high, by addition of excess TMPEO, the unreacted alcohol adds to the dielectric constant. Unreacted TMPEO can also act as mobile charge carriers in the dielectric if they are not bound to the crosslinked matrix.

Lithographic evaluation.— The positive results from the mechanical and electrical measurements by the TMPEO to the films merited a detailed study of the lithographic properties. QCM experiments were performed to evaluate the swelling behavior of the PNB films. Previous results showed that non-chemically amplified, positive tone PNB dielectrics readily swelled when exposed to aqueous base developer.[9] The presence of aqueous base in the film before curing can negatively impact the acid-catalyzed cross-linking reaction, so minimal swelling is desired. Formulations of PNB-C with 10 pphr TMPEO were coated onto QCM crystals and processed in the same way as described above. The unexposed films were baked at 140°C (the PEB temperature) for various times and developed in a QCM flow cell for 90 s with aqueous base. Figure 7 shows the QCM traces of normalized mass change with respect to time. Prior to the experiment, water flowed through the flow cell so that a sharp air-to-liquid transition was not seen when the sample was exposed to the developer. At time zero, a valve in the flow path was switched from water to TMAH. This resulted in TMAH reaching the sample at approximately the 10 s mark. As seen in Figure 7, the samples baked for 30 and 60 s exhibited little or no mass change as a result of the TMAH. However, samples baked for 120 s and 240 s slowly dissolved (the mass decreases) upon exposure to TMAH. For reference, fully exposed samples developed within 15 s of contact with TMAH. This dark erosion (i.e. development of the unexposed regions) is unusual since the 140°C bake temperature should not be hot enough to cause thermal degradation of the tert-butyl ester

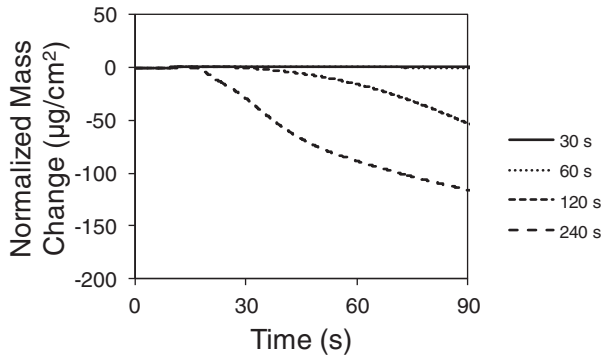

Figure 7. QCM traces of PNB-C with 10 pphr TMPEO baked at 140°C for various times.

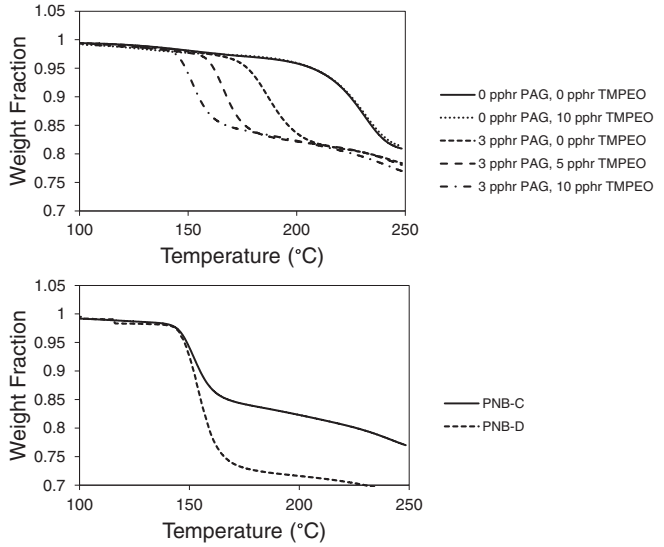

Figure 8. TGA traces of (top) PNB-C films with various additive loadings and (bottom) PNB-C and PNB-D with 3 pphr PAG and 10 pphr TMPEO.

or the PAG. Similar QCM experiments were performed with a PNB-C formulation without any TMPEO. It was found that this formulation exhibited no dark erosion even when baked for 240 s at 140°C. This shows that TMPEO affects the solubility of the protected polymer. The effect of the PEB time on the solubility of the polymer suggests that a reaction is occurring.

The thermal stability of the PNB-C with various loadings of TMPEO and PAG was investigated using TGA. The TGA traces are given in Figure 8. The base polymer without any additives decomposed at 212°C. This is an appropriate temperature for the thermal deprotection of TBENB. Additionally, the loss of 15% to 20% of the overall mass was expected based on the mass of isobutylene released during the deprotection of TBENB. When TMPEO was added to the PNB-C, no change in the deprotection temperature was observed. Next, a film of PNB-C was analyzed that had 3 pphr PAG. In this film, the deprotection occurred at 176°C, which is approximately the temperature at which the PAG thermally decomposes. Once PAG decomposition occurs, a strong acid is generated that can catalyze the deprotection reaction. When 3 pphr PAG and 5 pphr TMPEO were added to PNB-C, the deprotection temperature shifted to 160°C, a lower temperature than PAG or TMPEO alone. Finally, a film of PNB-C with 3 pphr PAG and 10 pphr TMPEO exhibited a deprotection temperature at 145°C.

The same TGA experiment was also performed with a film of PNB-D loaded with 3 pphr PAG and 10 pphr TMPEO. This film exhibited the same deprotection temperature as the PNB-C film with the same loadings, indicating that HFANB is not participating in the reaction. It is hypothesized from these QCM and TGA results that the TMPEO lowers the decomposition temperature of the PAG. Crivello et al. found that the diaryl iodonium PAG is reduced during the decomposition reaction, and the products can lower the energy required for the deprotection reaction.[16] It is likely that TMPEO acts as a reducing agent in this system, and the decomposition temperature of the PAG depends on the concentration of TMPEO. The QCM and TGA results correlate well for formulations with 3 pphr PAG and 10 pphr TMPEO. Even though there is a slight temperature discrepancy between the hot plate and the TGA, the 140°C PEB is very close to the observed deprotection temperature. It is likely that the 140°C PEB causes a small amount of deprotection of the PNB-C that imparts solubility in the aqueous base developer.

Based on the results given above, the PEB time was kept at 60 s. It is noted that dark erosion could also be mitigated by lowering the PEB temperature or reducing the amount of TMPEO, but these were not explored. The contrast and sensitivity of PNB-C with 3 pphr PAG, 10 pphr TMPEO, and 1 pphr CPTX were measured using a

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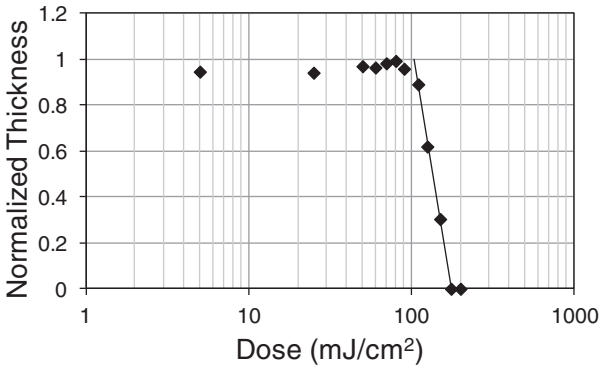

Figure 9. Contrast curve of PNB-C with 3 pphr PAG, 10 pphr TMPEO, and 1 pphr CPTX.

1.48 μm film. The films were exposed at 365 nm and the resulting contrast curve is plotted in Figure 9. The sensitivity (D_{100}) of this formulation was measured to be 175 mJ/cm^2, which is significantly higher than the same PNB dielectric without plasticizer at 248 nm (8.09 mJ/cm^2).[6] This can be attributed to two factors. First, 248 nm radiation directly activates the PAG, whereas exposure at 365 nm requires an inefficient energy transfer between the CPTX and PAG. The second, the TMPEO introduces excess water into the film before exposure. The excess water forms a hydrated hydronium ion when the PAG is exposed rather than the stronger acid which would exist in the absence of excess water. The hydronium ions catalyze the deprotection reaction at a slower rate, resulting in a loss of sensitivity. The water from the film can be removed during the high temperature bake which mitigates its effect on other properties such as dielectric constant. The PEB has a limited temperature and time range because of the above mentioned PAG/TMPEO reaction. The contrast of this formulation was measured to be 4.36. It is noted that both the sensitivity and contrast are better than existing positive tone dielectrics.[7,8]

SEM micrographs of patterned films are shown in Figure 10. Since soft contact photolithography was employed, diffraction limited the minimum feature size achievable. The top and middle images in Figure 10 show 50 μm and 16 μm half-pitch trenches, respectively, in a 4.5 μm film, exposed at 360 mJ/cm^2. The bottom image shows 16 μm half-pitch hills in the same 4.5 μm film, exposed at 225 mJ/cm^2. It can be seen that both hills and trenches have nearly vertical side-wall profiles. Exposure of this film with an appropriate photolithography tool could enable high aspect ratio features. Since the deprotection of TBENB produces gaseous isobutylene and the esterification crosslinking produces water, curing will result in a volumetric shrinkage of the features. This will change the feature dimensions to have wider openings at the top of the film and exhibit slight sidewall sloping. This profile is attractive for void-free electroplating of copper, and the angle of this sloping can be modified by varying the TBENB molar ratio.

Figure 10. SEMs of 50 μm trenches (top), 16 μm trenches (middle), and 16 μm hills (bottom).

Conclusions

A chemically amplified, positive tone dielectric has been developed with excellent mechanical, electrical, and lithographic properties. This dielectric was a copolymer of HFANB and TBENB. Two methods were evaluated for modifying the mechanical properties in an effort to form thicker films. First, ButylNB was added as a third monomer to the polymer backbone. The substitution of HFANB/TBENB with ButylNB resulted in a lower elastic modulus. Unfortunately, this substitution also increased the dielectric constant. Second, plasticizing additives were mixed with the HFANB/TBENB copolymer. Five additives were investigated and it was shown that TMPEO produced highest quality films which had a lower elastic modulus. TMPEO enabled the deposition of thick films (>5 μm) on silicon. In addition, films with TMPEO loadings of 10 pphr or less had a 2.76 to 2.94 dielectric constant, which is of interest for electronic packaging and interconnect. The dissolution behavior of an optimized formulation was evaluated, and it was found that TMPEO decreases the deprotection temperature of TBENB, likely by lowering the decomposition temperature of the PAG. The sensitivity and contrast of a formulations with 10 pphr TMPEO were measured to be 175 mJ/cm^2 and 4.36, respectively. Finally, a patternable, 365 nm sensitivity, thick film dielectric was demonstrated with nearly vertical sidewall profiles.

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